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Published in:
Journal of Membrane Science

DOI:
10.1016/0376-7388(94)00117-0

Publication date:
1994

ELSEVIER

Journal of Membrane Science 95 (1994) 105–123

journal of MEMBRANE SCIENCE

Review

Current hurdles to the success of high-temperature membrane reactors

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Received 28 October 1993; accepted in revised form 19 May 1994

Abstract

High-temperature catalytic processes performed using inorganic membranes have been in recent years a fast growing area of research, which seems to have not yet reached its peak. Chemical engineers, catalysts and materials scientists have addressed this topic from different viewpoints in a common effort. Despite the amount of work already carried out, the direct application of inorganic membrane reactors in the process industry is still limited because of a large number of technical and economic drawbacks.

The opportunities of this novel type of reactor compared with conventional reaction and separation systems have been emphasised in several former reviews. In the present contribution attention is focused on the major hurdles along the way of exploitation of these possibilities: high costs, low permeability, synthesis of defect-free permselective layers, instability of membranes and catalysts, sealing of membranes into modules, etc. An assessment of what has been already accomplished in the attempt to overcome these limitations is given, stressing the gaps still to be filled and pointing the way towards future efforts to reach this goal.

Keywords: Membrane reactors; Catalysis; Inorganic membranes

1. Introduction

The idea of coupling a chemical reaction and a separation by a membrane, so as to increase the conversion of equilibrium-limited reactions, dates back to the 60s [1]. Since then polymeric membranes have been used for this purpose in a number of studies mainly in the biotechnological field, where some practical applications could be successfully exploited [2].

Gas–solid catalytic processes imply temperatures ranging from 200 to 600°C. Below 200°C the reaction rate is generally too low, while above 600°C most of the catalyst supports undergo unacceptable sintering. These temperatures hamper the use of polymer membranes. For high-temperature catalytic membrane reactors, inorganic membranes remain the only candidates, though by far less developed and commercialized than their organic counterparts. In particular, ceramic membranes have seen an enormous development in the last years due to successful improvements attained in several manufacturing techniques (i.e., sol–gel, pyrolysis of poly-

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0376-7388/94/$07.00
SSDI 0376-7388(94)00117-H

meric precursors, phase separation and leaching, etc.) [3]. This made them potentially interesting either as high-temperature gas separators or as supports for more permselective, though generally less permeable, metal membranes. Table 1 lists pros and cons of ceramic membranes versus polymeric ones. Further, an entire volume has been recently published on inorganic membranes, their manufacture and applications [4].

Using these membranes, either catalytically active or enclosing a conventional fixed bed of catalyst pellets, a number of reactions have already been proposed and tested. Table 2 lists those of major importance for the petrochemical industry, the most interesting area of potential application. A much wider survey of reactions performed on high-temperature membrane reactors is provided in [5].

Apart a few attempts to apply inorganic membranes to phase-transfer catalysis in gas–liquid–solid systems [6–9] most studies have been focused on gas–solid heterogeneous catalysis, aiming either at increasing the conversion of equilibrium-limited reactions, or at enhancing the reaction selectivity towards desired products (Table 2).

Table 1
Advantages and disadvantages of ceramic membranes versus polymeric ones

Advantages
Long-term stability at high temperatures (in any case lower than those reached during the firing step of their manufacture)
Resistance to chemicals (organic solvents, wide pH ranges, detergents, steam, etc.)
Mechanical stability up to high pressure drops (> 30 bar)
Stability to microbial degradation
Long lifetime
Easy cleanability (steam sterilization allowed, high backflushes can be used to reduce fouling)
Catalytic activity is relatively simple to be promoted
High throughput fluxes are attainable when operating with high pressure drops
Disadvantages:
High capital and repair costs
Brittleness (special handling procedures and supporting systems are needed)
Low surface area to module volume ratios feasible
High selectivities available only on a few laboratory-scale membranes
Membrane sealing into modules difficult at high temperatures

Table 2
Some reactions of potential interest for inorganic membrane reactor application in the petrochemical industry

	Ref.
Conversion enhancement (equilibrium-limited reactions)	
Methane steam reforming	[10–15]
Ethane dehydrogenation	[15–19]
Propane dehydrogenation	[12,20]
Cyclohexane dehydrogenation	[15,21,22]
Ethylbenzene dehydrogenation	[23–26]
Water-gas shift reaction	[19,27–29]
Selectivity enhancement	
Oxidative coupling of methane	[19,30–33]
Partial oxidation of propane to acrolein	[18]
Partial oxidation of butane to maleic anhydride	[18]
Partial oxidation of ethene	[18,34]
Partial oxidation of butene to methacrolein	[35,36]
CO hydrogenation to hydrocarbons	[18,37,38]

In this last context, potential benefits to selectivity may arise because:

a. the membrane keeps the bulks of the two reactants separated, avoiding their pre-mixing and the consequently promoted side reactions [39];
b. the membrane (dense in this case: Pd alloys, solid electrolytes, etc.) can supply one of the reactants (the permeating species: O, H, etc.) in a monatomic form, particularly active towards, for instance, partial oxidations [40], or partial hydrogenations [41,42];
c. the membrane (porous in this case: γ-Al_2O_3, Vycor glass, etc.) modifies in an advantageous way the residence times and the concentration profiles of the reactants in the catalytically active zone [43–46]; or
d. the membrane is permselective to an intermediate product of a series of consecutive reactions [47,48].

In all these cases, most of the times analysed mainly by means of modelling (as for point d) or for very particular reaction pathways [49], the potential advantages highlighted have been rather

limited. As a result it seems quite difficult that membrane reactors could outperform traditionally employed reactors for this kind of application on an economic basis.

Suitable membranes for exploiting the properties listed in points a, b and c are already available or, at least, could be manufactured without major problems at the present technological level (permselectivity is not required or in any case not essential for these applications). However, the capital investment they imply would likely be too high compared with the slight advantages they may guarantee.

Finally, as regards point d, the authors themselves [47] admit that synthesising membranes permselective towards reaction intermediates would be quite a difficult task, requiring the imaginative use of particular transport mechanisms (i.e., capillary condensation, surface diffusion, etc.). Most of the currently available membranes separate smaller molecules from bigger ones according to Knudsen diffusion. For instance, during partial oxidations the Knudsen regime favours the permeation of oxygen and of complete oxidation products (CO_2, H_2O) instead of partial oxidation ones (except for CO).

Therefore the most promising field of application for inorganic membrane reactors remains the circumvention of chemical equilibria, where the membrane permselectivity is essential. However, a number of obstacles still stand along the way to practical application.

Several reactions carried out in the process industry are conditioned by chemical equilibrium. This implies only limited conversions per pass at operating conditions that are generally chosen according to a compromise. Dehydrogenations, for instance, are favoured by high temperatures and low pressures, but above a certain temperature limit structural and catalytic materials are affected, or unacceptably fast side reactions take place. Conversely, too low pressures imply too large reactor volumes.

Fig. 1 shows a simplified scheme of the traditional process for styrene production [50]. Similar setups are encountered for other industrial-scale dehydrogenations (e.g., butene production [51]). It is a relatively well-established technology whose main characteristics are the pre-heating of ethylbenzene with steam (also added to the reactant in order to prevent cocking), the adiabatic fixed-bed reactor and the wide separation section (the products are purified and the unconverted reactant is recycled). Variations are possible in the sequence of the distillation columns as well as in the design of the reactor. Conversion per pass is ~60%, with a 90% selectivity.

If a completely permselective membrane reactor could be used in this process:
- conversion per pass might be increased up to completeness, which would imply the absence of ethylbenzene recycle and a consequent reduction of energy consumption (re-heating), as well as in a simplification of the separation section;
- pure hydrogen would be directly obtained at one side of the membrane; and
- equal conversions would be achieved at lower temperatures, with a possible benefit for the selectivity, or at higher mean pressures, thus reducing the reactor volumes.

However, if the membrane is not permselective enough:
- conversions cannot be driven to completeness (some reactant accompanies hydrogen in the permeate side);
- reactant recycles are unavoidable;
- the separation is not simplified, if not complicated by the fact that two outlet streams, from the reactant and the permeate side, have to be dealt with; and
- the advantages either in conversion enhancement, or in temperature lowering, or in pressure rising are limited.

Therefore in order to fully exploit the potentials of inorganic membrane reactors, highly permselective membranes have to be used, which moreover should have sufficient permeability, high thermal, chemical and mechanical stability, a proper catalytic activation, a suitable module design and engineering, and a conveniently low cost. Such membranes are not yet available, and probably they will not be available in the near future. A number of researchers (chemical engineers, catalysts and materials scientists) are working on this all over the world; each one has

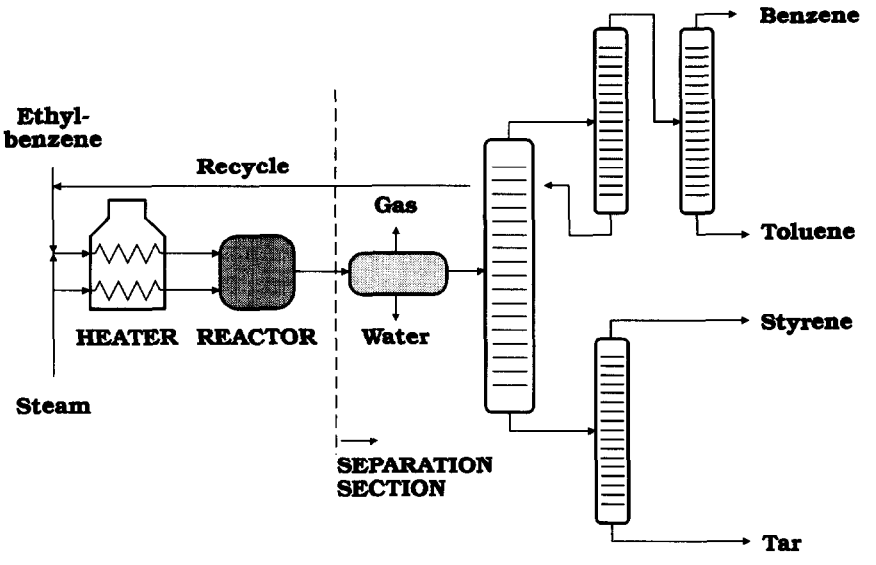

Fig. 1. Scheme of a traditional plant for ethylbenzene production.

to face serious challenges in his own field.

Formerly published reviews have particularly addressed the potentials of membrane reactors, the manufacturing routes and the properties of inorganic membranes, the reactions tested, the catalytic aspects and the modelling of membrane reactors [5,42–57]. This review is focused on the above-mentioned challenges, offering an assessment of what has been obtained in the attempt to face them, and trying to point the way to overpass present limitations. The literature published until August 1993 is considered.

2. Challenges for materials scientists

Materials scientists should address the most crucial topics concerned inorganic membranes: permselectivity, permeability and thermochemical stability.

In the absence of competitive technologies, ceramic membranes have met extensive application in the separation of uranium isotopes in the nuclear industry, despite the quite low separation factors achievable ($\alpha = 1.004$) [4]. However, porous ceramic membrane reactors for equilibrium circumvention require much higher permselectivities to become practical. Pores should be narrower than 10 Å so as to enable highly selective mechanisms such as molecular sieving [54].

A first issue concerning so small pore dimensions regards their measurability. Methods like liquid-displacement permoporometry or nitrogen adsorption/desorption, often used for membranes of higher pore dimensions, cannot be reliably employed below 10–14 nm [58]. A rapid, reliable, and possibly non-destructive technique is needed to assist any further investigation concerned the attempt to get pores of molecular dimensions. In this context encouraging work is being carried on by modifying the adsorption/desorption method using helium instead of nitrogen [59]. Techniques based on NMR spin–lattice measurements show promise as well [60].

The lowest pore dimension available on commercial membranes is ~40 Å (e.g., Membralox γ-Al_2O_3 membranes by SCT, Tarbes, France). These membranes are produced through a sol–gel route in comparatively small amounts and exclusively for research purposes. On such membranes numerous dehydrogenations have been

tested getting promising though insufficient results [12,16,20,24–26,61–63].

Pore sizes down to ~ 10 Å have been achieved, only at laboratory scale, by the use of polymeric silica sols deposited on γ-Al_2O_3 supports [64,65]. Despite their high separation factors (up to 160 for C_3H_8/H_2 separation [65]) molecular sieving was not reached. Moreover, these membranes showed limited thermal stability and very low permeability. In fact, their porous structure arises, during calcination, from a collapse of the silica-gel deposited layer, resulting in a very low porosity.

A way to decrease the pore dimensions of a preformed layer could be the deposition of a second phase on the pore walls. Experimental tests lead also in this case to unsatisfactory results: permeability decreased, molecular sieving was not reached and the thermal instability of the membranes remained unsuitable for practical application [66,67].

In fact most of the materials used for the synthesis of ceramic membranes are metastable (e.g., γ-Al_2O_3). They undergo pore growth for prolonged use at such temperatures as those of interest for several dehydrogenations (500–600°C). Short lifetimes hamper the applicability of those membranes either as gas separators (with or without a reaction) or as supports for more permselective layers. Attempts were made to stabilise these structures at high temperatures [68,69]. Lin and co-workers [68], adding $LaNO_3$ as a dopant either in the promoting sol or directly into the membrane by impregnation with aqueous solutions, could shift the γ/α-Al_2O_3 phase transition from 1000 to 1200°C. At those temperatures pore dimensions were also stabilised at 250 Å, which is definitely a too high value.

Most hopes lie in the synthesis of zeolite membranes. Zeolites are crystalline; their pores arise from the lattice spacings (a few Å) of their molecular structure and should be stable until the crystalline structure itself remains unaffected.

An optimum condition would be having a single-crystal membrane: this would assure a complete absence of defects and a transport controlled only by molecular sieving. However, this is generally regarded as utopistic. Most studies in this area were indeed focused on manufacturing zeolite membranes by growing together several zeolite crystals or holding them together in a polymeric gas-tight matrix.

In this last case, the stability of the membrane is bound to that of the polymer used; therefore only low-temperature pervaporation applications were proposed and tested for such membranes [70,71].

Numerous experiences on growing together zeolite crystals were unsuccessful: the obtained crystals were not sufficiently close to each other, leaving gaps that controlled the separation according to the Knudsen regime [72–74]. Only very recently and in rare occasions, molecular-sieving effects were noticed on this kind of membranes [75,76]. These promising results were though obtained only on laboratory-scale membranes. Reproducing these membranes on large dimensions, suitable for industrial application, seems to be quite a difficult task. Moreover they show extremely low permeability, brittleness and low resistance to abrasion. This would require extremely careful handling and operating conditions so as to avoid any crack or defect formation. Depending on their dimension, due to the low permeability of the zeolite structure, defects would easily govern the overall separation properties and render large membrane areas almost ineffective.

Table 3 lists a collection of permeabilities for inorganic membranes for gas separation. As a rule, for porous ceramics, permeabilities become lower and lower as long as the pore size decreases and the permselectivity increases. A compromise must be found using multilayer-supported membranes, in which the separation is carried out on a very thin top layer, so as to get reasonable gas permeation rates, despite the low permeability.

This concept has been successfully applied since the 50s for polymer membranes thanks to manufacturing techniques (i.e., phase-inversion) which are capable of producing permselective layers of 1 μm or less deeply bound to a basic support. For ceramic membranes obtained by the sol–gel technique Ulhorn and co-workers [86] demonstrated that several subsequent deposi-

Table 3
A survey of permeabilities of inorganic membranes

Membrane material	Temperature (K)	Permeability (mol/m Pa s)	Gas	Ref.
Dense membranes				
Ag	675	$5.4 \cdot 10^{-16}$	O_2	[77]
Ag	1075	$2.0 \cdot 10^{-13}$	O_2	[77]
Pd	293	$1.2 \cdot 10^{-12}$	H_2	[4]
Pd	673	$5.7 \cdot 10^{-12}$	H_2	[54]
Pd–Ag(23%)	673	$1.7 \cdot 10^{-11}$	H_2	[54]
Pd–Y(7.8%)	573	$8.9 \cdot 10^{-11}$	H_2	[78]
SiO_2	723	$1.3 \cdot 10^{-15}$	H_2	[79]
Y_2O_3(8%)–ZrO_2	1073	$5\text{–}50 \cdot 10^{-18}$	O_2	[80]
Y_2O_3(25%)–ZrO_2	923	$1.7 \cdot 10^{-13}$	O_2	[80]
$SrCo_{0.8}Fe_{0.2}O_3$	923	$3.6 \cdot 10^{-12}$	O_2	[81]
$La_{0.79}Sr_{0.2}MnO_{3-\alpha}$	973	$5 \cdot 10^{-15}$	O_2	[82]
$La_{0.79}Sr_{0.2}MnO_{3-\alpha}$	1133	$5 \cdot 10^{-13}$	O_2	[82]
Porous membranes				
γ-Al_2O_3 (4 nm)	1000	$3 \cdot 10^{-12}$	O_2	[80]
γ-Al_2O_3 (3 nm)	293	$1.5 \cdot 10^{-11}$	H_2	[4]
γ-Al_2O_3 (4 nm)	295	$2 \cdot 10^{-11}$	H_2	[80]
Vycor glass	293	$1.1 \cdot 10^{-10}$	H_2	[83]
Vycor glass	293	$3.1 \cdot 10^{-11}$	O_2	[83]
Porous SiO_2 (<2 nm)	343	$9.5 \cdot 10^{-12}$	H_2	[84]
Porous SiO_2 (<2 nm)	473	$1 \cdot 10^{-13}$	H_2	[65]
Carbon (mol-sieve)	773	$2.4 \cdot 10^{-13}$	H_2	[85]

tions had to be performed so as to get defect-free γ-Al_2O_3 permselective layers, thus obtaining thicknesses of 3–5 μm for such layers. Since defects cannot be tolerated in gas separation applications [87], means to get much thinner and defect-free membranes have to be developed to achieve competitiveness, provided high permselectivities are also attained.

The same concepts hold for dense membranes (metals or solid electrolytes). Despite their almost absolute permselectivity, self-supporting membranes proved to be applicable for gas separation purposes only in small-scale units [88], owing to the extremely low permeation fluxes they allow.

The most studied metal membranes have been those made of Pd alloys, due to their comparatively high hydrogen permeability [55]. However, palladium becomes brittle and prone to distortions as a consequence of temperature cycling (reactor start-ups and shut-downs). This is due to the dimensional changes of the lattice structure, caused by the repeated transformation between the α phase (stable at low temperatures) and the β phase (stable at high temperatures) [54]. Some alloy elements (e.g., Ag, Ru, Rh) stabilise the β phase against the α phase thus reducing to some extent the problem of embrittlement [54]. Further work is needed to optimise the alloy composition for this purpose.

Thickness reduction of Pd alloy membranes is a major need not only for increasing the permeation fluxes but also for reducing costs that are proportional, in first instance, to the amount of

precious metal used. Quite interesting results have been recently gained through the electroless-plating technique [89,90]. Uemiya and co-workers [91,92], manufactured 20 μm thick Pd–Ag membranes deposited either on alumina or on Vycor glass supports. However, the stability of these membranes was poor: the α–β transition caused the formation of cracks, pinholes and distortions, limiting their lifetime. Chemical and mechanical interactions between metal membrane and ceramic support may also play a role in this context. Collins and Way [93] claimed they deposited 1 to 5 μm thick Pd membranes on γ-alumina supports. They also stated that these membranes could withstand, without delamination, a temperature cycle from room temperature to 600°C and back. However, no evidence was given that the permeation through these membranes was still controlled by the deposited Pd.

Nonetheless, the most surprising result remains the one reported by Gryaznov [94]: through a novel technique he could manufacture 2 μm thick Pd–Ru–In membranes (deposited on porous stainless steel), capable of withstanding 450 temperature cycles between room temperature and 400°C without defect formation. The support is first coated with indium, kept in the liquid state. After hardening, the other components are introduced by magnetron sputtering. However, it has to be underlined that this technique is by far less amenable for large scale production than electroless plating.

Finally, another fundamental problem hampering Pd membrane application in membrane reactors is their strong susceptibility to poisoning. CO and sulphur compounds, present in a number of gaseous streams, strongly chemisorb on Pd alloys affecting both their permeability and catalytic properties. At Bend Research Inc. (Bend, OR) new membranes are being developed, on the basis of composite structures of different metals (Pt, V), which are less sensitive to poisoning, but also less permeable, than Pd [27,95,96]. However, Govind and Zaho [97] stated that these membranes could be outperformed by solid electrolyte membranes based on proton conductors such as $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$. Solid electrolytes show generally a good thermochemical stability, but their permeability is very low unless rather high temperatures are employed (>800°C). The potentials offered by new materials (e.g., perovskites, see Table 3), showing comparatively higher permeabilities than the classical doped ZrO_2, have still to be fully assessed, especially as concerns the possibility of reliably depositing thin and stable films on porous supports [82].

In any case, being the membranes dense or porous, metallic or ceramic, thin supported structures seem to have much more chances than self-supporting ones, at least for applications concerning conversion increase for equilibrium-limited reactions. The support has to be porous, highly permeable, smooth, and mechanically resistant. Any surface defect of the support has to be avoided, because it would easily result in a defect of the membrane. Obtaining such a support is not a trivial task. Glez and co-workers [98] demonstrated that only following rigorous procedures one may obtain these desired properties. Most of the supports used for inorganic membrane layers have been ceramic ones. Some interest was though focused in recent years on porous metal supports. Limitations may arise in this case concerned the operating temperatures allowed: porous stainless steel can withstand only temperatures up to 450°C without appreciable modifications of the pore structures, while more expensive alloys, such as Monel or Hastelloy, can resist up to 600°C. However, porous metal supports show promise for a number of opportunities:

- they are resilient and have a good mechanical resistance;
- they have a high thermal conductivity that may be helpful when heat exchange occurs with the membranes (thermal conductivity can be as high as 10 W m^{-1} K^{-1} [99] against ~0.86 W m^{-1} K^{-1} typical of porous sintered alumina [100]); and
- they can be directly sealed into stainless steel modules.

More work should be addressed to further developing these potentials. Dealing with ceramic membrane layers additional problems may arise

due to the different expansion coefficients of the metal support and the membrane itself. Van Looij and Terörde [101], claimed to have overcome this problem by synthesising a defect-free SiO_2 membrane on a porous stainless steel support via pyrolysis of a polymeric precursor. In this way, after calcination, the membrane remains under compression. This helps to overcome the tensions arising from the higher expansion of the metallic support at high temperatures.

Analogous problems have to be solved when trying to seal ceramic supports into metallic modules. A variety of solutions have been attempted for this sake. After coating the membrane ends with some glass or enamel compound, sealing has been provided with different techniques:

- using polymer gaskets with localised cooling (polymers cannot withstand higher temperatures than 300°C [102]);
- employing graphite strings wrapped several times around the membrane ends, and pressed by compression fittings [63] (graphite is stable up to ~450°C in oxidising environments);
- combining ceramic adhesives/sealants and graphite ferrules [93]; and
- joining ceramics and metals through a multiple brazing technique [103].

This last solution, developed in particular by Velterop B.V. (Heerhugowaard, Netherlands), seems to be the most promising. The porous ceramic support is sealed with an inorganic adhesive to a dense ceramic ring. A metal bellow is applied on the ring through seven consecutive brazed layers of materials showing a fracture behaviour ranging progressively from brittle to ductile. A membrane carrying these ceramic-to-metal joints at both ends is shown in Fig. 2. However, this manufacturing technique is, at present, time consuming and thus rather expensive. A decrease of costs is expected in case mass production of these joints becomes viable. As a further improvement the same Dutch firm has recently patented a new sealing procedure: the porous ceramic support is directly coated at its ends with brazing material, obtaining a structure progressively varying from porous to dense, on which metallic connections can be directly applied [104]. This might be a good solution for reducing the unit cost of this type of connections.

Concerning flat membranes, it is much more difficult to obtain reliable brazed joints between the dense ceramic rings and stainless steel modules. In this case the dense ceramic ring can be sealed into modules using graphite gaskets. Fig. 3 shows a laboratory-scale module based on this principle.

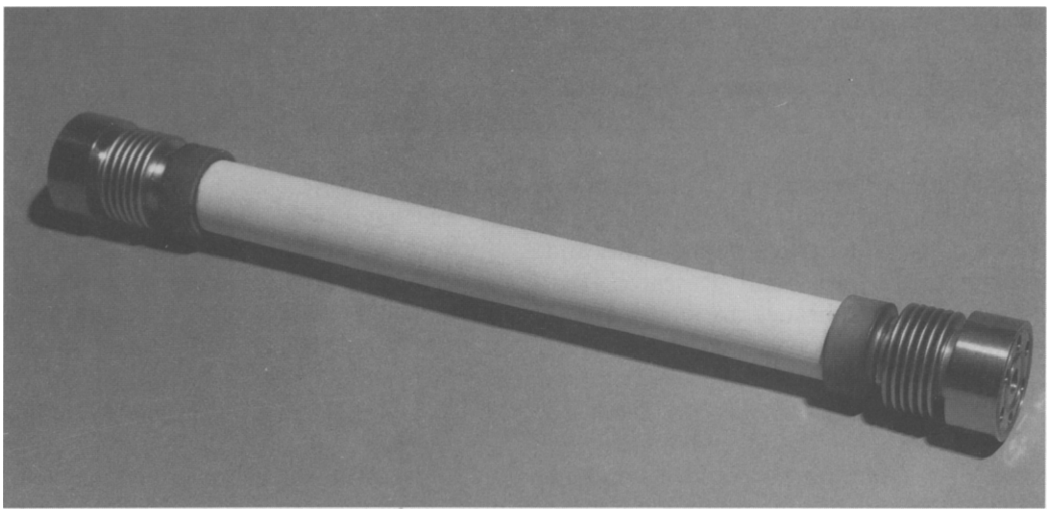

Fig. 2. A ceramic membrane provided with two ceramic-to-metal connections (courtesy of Velterop B.V.).

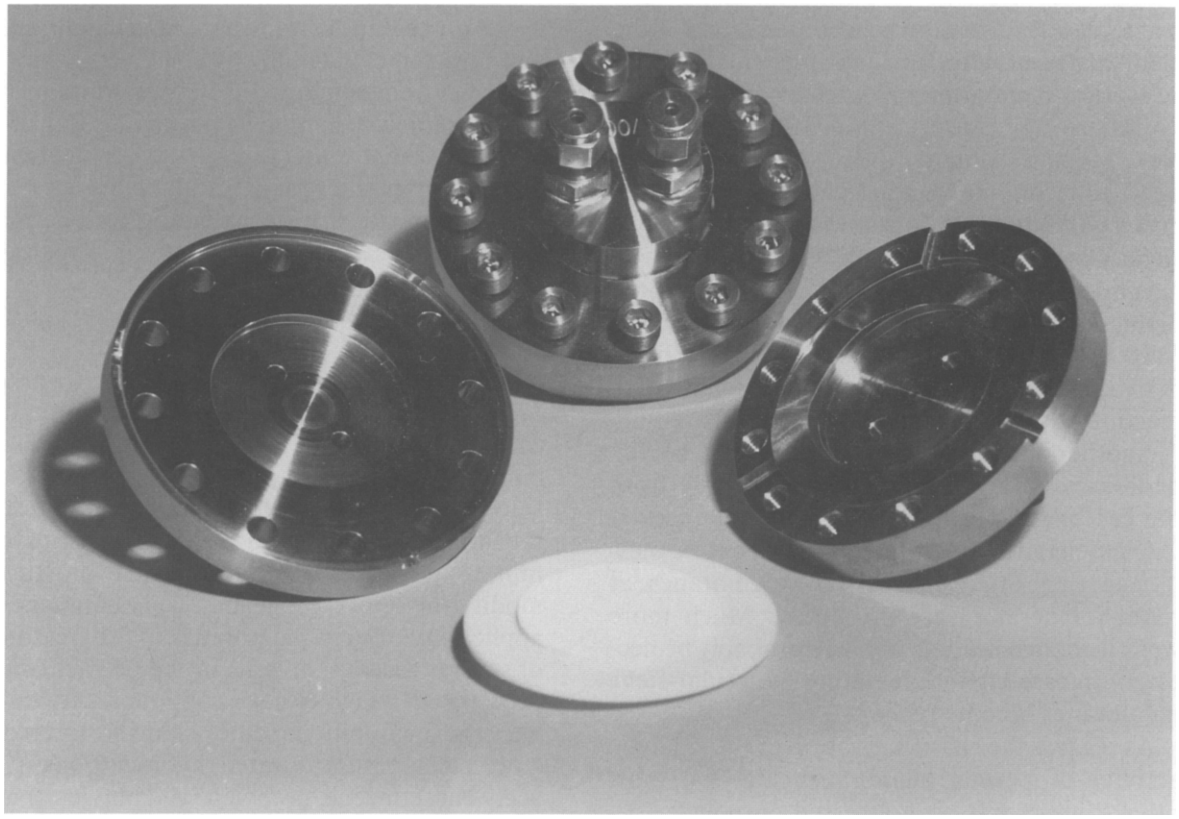

Fig. 3. A laboratory-scale module employing flat membranes (courtesy of Velterop B.V.).

3. Challenges for catalysts scientists

As regards catalysis on inorganic membranes, much more fundamental research is needed concerning:

a. the catalytic activation of membranes and its reproducibility;
b. the assessment of their catalytic properties (i.e., kinetic law, selectivity, etc.); and
c. the deactivation of membrane catalysts (i.e., temperature stability, poisoning, cocking, etc.).

Pd alloy membranes, and in some cases solid electrolyte ones, are intrinsically active. Their activity can be directly controlled, to some extent, varying their composition. A drawback of these catalysts is though their low active surface area per unit volume. This can be partially overcome by the deposition of further, finely dispersed catalyst on their surface, or by special chemical treatments leading to a highly corrugated surface, suitable for the deposition of catalytic material [105].

As regards the activation of porous membranes a critical point is getting the desired catalyst distribution along the membrane thickness, without affecting the membrane structure and permeation properties (i.e., defect formation, excessive pore obstruction or plugging). Both theoretical [106] and experimental [107] studies proved that the catalyst distribution in a membrane may play a role in controlling both selectivity and conversion levels for a variety of reactions.

When a sol–gel technique is employed for membrane manufacturing, a catalyst can be either added to the promoting sol [108], or deposited afterwards. In this last case, techniques based on classical wet deposition [109] may give

rise to defect formation as a consequence of the heat treatments needed for the calcination and activation steps. Some researchers of the Center for Microengineered Ceramics (University of New Mexico, Albuquerque, NM) have developed a technique for activating (homogeneously, without defect formation, and with only a slight decrease in permeability) sol–gel derived ultramicroporous silica membranes (mean pore diameter ~ 10 Å) deposited on γ-Al_2O_3 supports [110,111]. This technique is based on an amine derivatization with a silylation agent, followed by reaction with metal–organic compounds.

Another interesting technique might be the deposition of active components directly from the gas phase. Preliminary results obtained by Capannelli and co-workers [112] about Pt-mesitylene deposition on γ-Al_2O_3 membranes at room temperature are promising. Much more work is though needed, and will probably be necessary in case high-temperature molecular-sieve membranes become practical.

As regards the characterisation of the catalytic activity of porous membrane catalysts, most often kinetics has been assessed on powder derived from membrane crashing. This is of course a first-approximation approach, whose main advantage is its simplicity. However, a number of new catalytic surfaces, formed during crashing, might play a role in conditioning the reaction evolution. From this viewpoint a better approach was that of Tsotsis and co-workers [19] who assessed the kinetics of ethane dehydrogenation on a Pt-activated γ-Al_2O_3 tubular membrane reactor, by closing the shell side of their module and letting the reactant flow in the tube side. Some other imaginative solutions may eventually be found. It seems, however, difficult to let the system be completely kinetic-controlled, so as to measure the intrinsic kinetic parameters.

Concerning Pd alloy membranes Armor and Farris [113] showed how the catalytic properties are extremely sensitive to activation and operating procedures. Results are often almost unpredictable. Much more fundamental work is here needed before attempting any application in the process industry, where reproducibility is a conditio sine qua non.

As mentioned before, Pd alloy membranes are also extremely sensitive to poisoning. CO, H_2S, SO_2 and several other compounds dramatically affect their permeability, catalytic activity and stability. A critical stage governing both permeation and reaction processes is hydrogen chemisorption:

$$H_{2(gas)} = 2H_{(chemisorbed)}$$

According to Al-Shammary and co-workers [78], this chemisorption takes place at certain active points of the membrane surface. These points are especially prone to contamination, since the relative activation energy of the rest of the surface is considerably higher. Because of this, minute quantities of impurities can drastically modify the above properties. This hampers the application of such membranes to the treatment of several gaseous streams in the petrochemical industry, in which either gas-borne reactive species (i.e., sulphur, arsenic, chlorine, mercury, zinc, etc.) or unsaturated hydrocarbons (i.e., acetylene, ethylene, propylene and butylene) may act as contaminating agents.

Though less permeable than Pd alloy ones, the aforementioned membranes developed at Bend Research Inc. (based on metals less sensitive to poisoning: Pt, V, Ti, etc.) are planned to be more serious candidates for membrane reactor application in the petrochemical industry [27].

Both metal and porous ceramic membranes are frequently affected by coke deposition when dehydrogenations of hydrocarbons are operated. Coke formation is generally favoured at high temperatures as a consequence of a number of endothermic side reactions. Sometimes the acidic nature of some of the membrane constituent (e.g., γ-Al_2O_3) catalyses these reactions [25]. Tsotsis and co-workers [16] showed how the hydrogen depletion in the reaction zone, due to the permeation of this gas through the membrane, could enhance coke formation during dehydrogenation reactions. In particular, during propane dehydrogenation runs, they had to feed hydrogen to the reactant mixture so as to keep coking at an acceptable level.

The possibilities to limit coking are substantially two:
- dosing to the reactant mixture an additional component which can react with the deposited coke; and
- preparing a new class of catalysts less sensitive towards coking.

As regards the first point, oxygen or steam have been frequently used. However, oxygen may directly react with the compounds to be dehydrogenated, thus promoting the formation of new, undesired chemical species. Steam demonstrated to reduce the membrane lifetime. In fact, in case of catalytically activated γ-Al_2O_3 membranes at high temperatures, steam catalyses the transition from the metastable phase to the thermodynamically stable α-Al_2O_3, giving rise to pore growth [62,114]. Moreover, at Alcoa laboratories [25] it was noticed, during ethylbenzene dehydrogenation on a γ-Al_2O_3 membrane reactor, that steam could only limit coke deposition at a regime level that, in any case, reduced the membrane permeability from 70 to only 2 m^3 m^{-2} h^{-1} atm^{-1}!

Therefore, for the limitation of coke formation, most hopes lie in the synthesis of membrane catalysts that are intrinsically less sensitive to coking. For example, Matsuda and coworkers [115], during isobutane dehydrogenation on a Pd membrane reactor enclosing a fixed bed of Pt–Al_2O_3 catalyst pellets, noticed that the addition of tin to Pt–Al_2O_3 could almost suppress coke formation, despite a slight decrease in catalytic activity. Further work is needed in this area.

Finally, due to the high costs of catalytically active membranes, they should be recovered once deactivated because of either catalyst poisoning or sintering or defect formation. This is especially true in case expensive and definitive sealing systems are employed (i.e., ceramic-to-metal connections).

4. Challenges for chemical engineers

Once suitable membranes will be available for high-temperature application, chemical engineers will have to optimise the design and the operating procedures of this novel kind of reactor.

First of all a suitable configuration of the reactor will have to be chosen. Fig. 4 shows some possibilities for this purpose.

Flat membranes can be easily stacked onto one another (Fig. 4a). Membranes can be kept separated using corrugated plates [6,94]. Such a system has been used at the Jet Propulsion Laboratory (California Institute of Technology, Pasadena, CA) for the purification of O_2 via solid-electrolyte membranes (Y_2O_3·ZrO_2) at high temperatures [116]. The major technical problem was the sealing of membranes into modules. The oxygen losses due to non-perfect connection (provided through precision grinding) was the main cause for the failure of this O_2 production system compared with other technologies. Moreover, modules based on flat membranes cannot guarantee, at present, surface areas per unit volume higher than 30 m^2/m^3, which is quite a low value compared to those attainable with polymer membrane modules [4]. Polymer membranes can indeed be assembled into spiral-wound or hollow-fiber modules whose specific surface area can reach up to 1000 m^2/m^3. Dealing with inorganic membranes, these last module configurations have been attempted only for Pd alloy self-supporting structures, but we for-

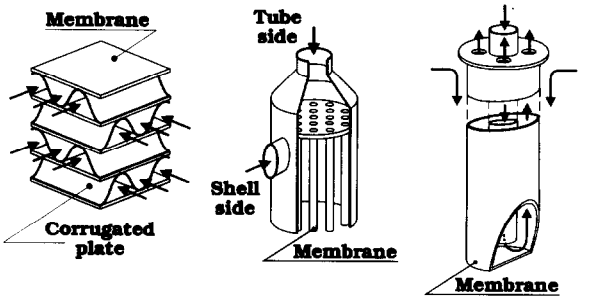

Fig. 4. Possible membrane reactor configurations: (a) flat membranes packed onto one another; (b) shell-and-tube module; (c) dead-end tube system.

merly showed how supported membranes are strongly suggested for reducing costs and increasing gas permeation.

Shell-and-tube modules (Fig. 4b) seem to be more promising since they can develop up to 250 m^2/m^3 [4]. Tsotsis et al. [57] stated that "industrial membrane reactors would most likely be composed of banks of tubular ceramic membranes, at least if the existing patent literature is to serve as an indication". The smaller the tube diameter the higher the specific surface areas attainable. However, attempts to manufacture hollow-fiber ceramic membranes were unsuccessful primarily because of brittleness problems [117–119].

In case sealing remains a major problem, the dead-end tube configuration (Fig. 4c) might be advantageous since it needs only one ceramic-to-metal connection. Drawbacks of this configuration are its higher pressure drops and the obvious limitations concerning membrane diameter reduction.

Most of the reactions that may eventually be performed in industrial membrane reactors would be endothermic. The enthalpy of reaction of most dehydrogenations is ~30,000 cal per gmol of hydrogen at 800 K [50]. This implies the need of heat supply based on either external firing or steam condensing systems. Temperature plays a primary role in governing the reaction kinetics and/or the thermodynamic limit to conversion. For cyclohexane dehydrogenation to benzene the equilibrium constant can decrease by 100 times when the temperature is lowered by only 40°C [56]. Heat losses due to permeation can affect seriously the overall conversion attainable, limiting, if not vanishing, the advantages related to the use of membranes. A recent study of KTI B.V. (Zoetemeer, Netherlands) on the feasibility of a ceramic membrane reactor based process for propane dehydrogenation showed how attractive improvements with respect to conventional processes could be achieved only if highly selective membranes are employed and heat is supplied to the reactor [120]. Temperature has thus to be kept homogeneous and high enough, provided coking would be tolerable, to get conveniently high conversions. Supplying heat to a high-temperature membrane reactor is not a trivial task. This may imply imaginative design solutions. For example, the above-described dead-end tube configuration might be helpful: the high-temperature inlet feed can indeed exchange heat with the relatively cold gas leaving the system, thus keeping a rather flat temperature profile along the membrane. Similar setups are employed in the industrial plants for ammonia synthesis [121]. Considerable experience in this field can be also derived from the design of various cracking furnace reactors [57].

Heat exchange between the two flows separated by the membrane will not be, in any case, negligible [122]. Configurations as those in Fig. 4 are typical of traditionally employed heat exchangers. For temperatures higher than 400°C, radiation can be more important than convection for heat-exchange purposes [10]. Finally, temperature profiles along the membrane thickness will be in any case rather small due to the comparatively high thermal conductivities of the partially sintered support structures.

Additional features to be considered in the design of industrial scale membrane reactors are [57]:

- the optimal sizing of these reactors in terms of membrane length, tube diameter, membrane thickness, number of membranes, etc.;
- deciding whether reactor staging, permeate or feed-side stream recycling, multiple or intermediate feed are advisable or not; and
- choosing proper flow patterns (i.e., countercurrent, cocurrent, etc.).

This last issue will be critical only in case permeation flow rates are comparable with those flowing along the membranes. A cocurrent scheme or the use of recycling can limit reactant permeation due to back diffusion, while a countercurrent scheme can drive conversion to completeness, provided the permselectivity of the membranes is perfect.

Due to the relatively low permeability of the membranes one may guess that the feed flow rates of membrane modules would be rather low (low Reynolds numbers). This will give rise to a laminar flow regime, which implies on the one hand

lower pressure drops per unit membrane length than turbulent flow, but on the other hand a much higher heat and mass transfer resistance toward the membrane itself, which may affect the performance of these reactors.

When coupling membranes and fixed-bed reactors, the position of the membranes in relation to the fixed bed has to be optimized, too. Especially in the first part of the catalytic reactors, where conversion is still markedly below the equilibrium level, the use of membranes can be detrimental rather than beneficial, due to important reactant permeation [10,26].

A further issue to be considered is the need to use large amounts of sweep gas to take away permeated products, thus driving equilibrium-limited reactions to higher conversions. The use of any other gas than air or steam would likely be too expensive. However, as already remarked, oxygen can interfere with the reaction performed generating undesired products, while steam affects the stability of several membrane constituents at high temperatures [62].

From the modelling standpoint good adherence to experimental results has been achieved in a number of laboratory-scale studies despite problems due to temperature control along the membranes, to coking or catalyst deactivation, or to modification of the pore structure (growing of pores at high temperatures) [57]. More serious problems will have to be faced on industrial scale reactors for which several assumptions usually made for small-scale membrane reactors will not hold anymore (plug-flow behaviour, isothermal or adiabatic conditions, absence of axial concentration gradients, etc.). This complex modelling still has to be developed to a great extent.

Finally, further research efforts have to be addressed to the study of highly selective transport mechanisms (surface diffusion, multilayer diffusion, capillary condensation, molecular sieving) which will affect transport in membranes having pores smaller than 10 Å [123,124]. Even though for some of these mechanisms predictive formulation has been attempted, the reliability of the derived formulas is still too low for a confident modelling.

5. Some economic remarks

Currently produced ceramic membranes are 3–10 times more expensive than polymer membranes [3,53,125]. Pd alloy membranes are even much more expensive. Armor and Farris [113] reported of a cost of US$1700 for a 0.25 μm thick 10×10 cm sheet of Pd–Ag(30)–Ru(2); Guy [15] declared a cost of F.Fr.250,000 per square meter for a 0.1 mm thick foil of Pd–Ag alloy. γ-Al_2O_3 multilayer membrane tubes (length: 25 cm; external diameter: 1 cm; thickness 1.5 mm; pore size: 4 nm) produced by SCT (Tarbes, France) cost about F.Fr.300 each, while a 0.5 mm thick 5×5 cm sheet of Vycor glass by Asahi Glass (Tokyo, Japan) costs US$35.5.

Most hopes in trying to lower prices of Pd alloy membranes lie in the reduction of their thickness using supported structures, as already mentioned. The support will likely be a mesoporous ceramic (20–500 Å pores), thus progress in the field of ceramic membranes is of major interest for use either as supports or as separators.

In 1989 the world market of ceramic membranes was about US$31·10^9, of which US$28·10^9 for micro- and ultrafiltration applications [126]. Crull [127] estimated for the end of this century a market of US$432·10^9 including US$80·10^9 for gas separation, primarily in the refineries. No need to say that this last prediction is bound to the large-scale development of more permselective membranes than the ones already available.

We showed how ceramic membranes have distinctive properties compared to polymer ones (see Table 1). Particularly, for microfiltration applications they are reported to outperform polymeric membranes by a factor 5–10, outlasting them by a factor 2 [125]. These advantages made them cost effective for a number of applications. However, for a penetration in novel fields as gas separation, production and replacement costs have to be further reduced.

Since production costs are likely to be sensitive to the production volume, costs should drop as long as inorganic membranes become more widely used [122].

According to Chan and Brownstein [18] this

can be reached only if inorganic membrane producers form strategic alliances in order to reduce risks and try to get a deeper penetration in the market. Joint ventures should be formed so as to discuss in a common effort issues connected to the engineering design, the manufacturing, the distribution and the after-sell service of ceramic membranes.

In fact, the separation business is at present dominated by a relatively small number of large international companies, often highly integrated and skilled from both technical and marketing viewpoints.

The above researchers also stress that in the pioneering area of gas separation and reaction at high temperatures additional government funding is needed to sustain research for the improvement of actually produced membranes from the standpoints of better controlled and finer pore size, chemical and thermal stability, and fracture toughness. This may be too riskful for the small-scale producers of ceramic membranes.

6. Conclusions

Inorganic membrane reactors combine in a single unit reaction and separation at high temperatures to increase the conversion of equilibrium-limited reactions or to potentially improve the selectivity of some partial oxidation or hydrogenation reactions. In this review we showed that major technological advances are still needed to fully exploit these opportunities at industrial scale.

Table 4 points the way towards future research efforts, summarising most of the above-discussed critical issues to be addressed by either chemical engineers or catalysts or materials scientists.

Materials scientists will definitely have a primary role in this context. The success of high-temperature membrane reactors mainly depends on whether highly permselective, sufficiently permeable and stable membranes will be manufactured or not. The urgency of the tasks for catalysts scientists and chemical engineers will depend, to some extent, on this.

Table 4
Major challenges in the development of inorganic membrane reactors

Materials science
Synthesising defect-free and homogeneous membranes having pores of molecular dimensions (< 10 Å)
Reducing the membrane thickness ($\ll 10\ \mu m$) so as to keep gas permeation acceptable
Reproducing the above results on large scale membranes
Working out reliable, quick, non-destructive analysis techniques to measure pore diameters lower than 10 Å
Improving membrane resistance to temperature and thermal fatigue
Addressing problems of brittleness for both ceramic and Pd alloy membranes
Improving chemical stability of inorganic membranes
Developing relatively cheap high-temperature sealing systems
Reducing membrane initial and replacement costs
Finding new materials with better properties than Pd, γ-Al_2O_3, etc.
Catalysts science
Developing new membrane catalysts less sensitive to poisoning or cocking
Getting a better reproducibility and predictability of the catalyst performance (especially for Pd alloys)
Getting a better control of the catalytic activation of ceramic porous membranes
Finding a reliable non-destructive way to assess kinetic laws for porous membrane catalysts
Chemical engineering
Understanding and modelling highly selective transport mechanisms
Increasing the membrane area per unit volume
Developing complex modelling for large-scale membrane reactor modules
Developing technologies for heat supply and temperature control in large-scale modules
Finding alternative solutions to eliminate the use of large amounts of sweep gas
Developing criteria for the choice of the optimal size of membrane reactors, of the flow patterns and of the number of stages/recycles/intermediate feeds

In any case there is no need to continue studying new reactions on currently available membranes; it is quite clear that the huge amount of literature appeared concerning this aspect lead to nothing more than promising results.

Acknowledgements

The authors gratefully acknowledge the financial support of MPI 60% (Ministero Pubblica Istruzione-quota 60%).

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